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Role of magnesium ions in reducing high temperature aqueous corrosion of carbon steel

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ABSTRACT

Carbon steel is used as the primary heat transport system piping material in pressurized heavy water reactors. The carbon steel surfaces corrode during the high temperature operation. Enhanced wall thinning of the piping in locations of high velocity and neutron activation of corrosion products pose serious operational difficulties. Magnesium ion modified water chemistry resulted in significant reduction in the corrosion and corrosion release of carbon steel. The changes induced by magnesium ions in the various processes at the metal–oxide, oxide–solution interfaces, and subsequent restructuring of the oxide were identified by in situ electrochemical impedance spectroscopy.

1. Introduction

Carbon steel is widely used as the construction material in the primary heat transport (PHT) system of Pressurised Heavy Water Reactors (PHWRs). Carbon steel, ASTM A106 Gr-B or ASTM A 333 Gr-6 is used for the primary coolant system piping. The carbon steel piping in the PHT system can be broadly classified into two sections, one carrying the hot coolant at 290 °C to the steam generator and the other carrying the coolant at 240 °C back to the reactor core. The carbon steel surfaces and other structural materials corrode during the high temperature operation. Corrosion of the carbon steel surface in the PHT system depends on the coolant parameters like dissolved iron content, temperature, pH and local velocity conditions [1]. This corrosion leads to two problems: radioactivity build-up in the primary heat transport system due to activation of corrosion products in the reactor core and wall thickness reduction termed as flow accelerated corrosion (FAC) in certain areas of the carbon steel piping, where the fluid velocity is high. The first one results in exposure of personnel to high radiation field during maintenance work [2,3]. The second one necessitates frequent replacement of affected piping and severely impairs plant life extension. Efforts are on worldwide to develop new structural materials, and to frame strict control regimes to mitigate these phenomena. As far as a running plant is concerned, there is very little scope of changing the composition of the structural materials other than a few components. Even design modifications would be difficult to implement and they require extensive downtime of the plant. Hence, with these operating plants, one is left with the choice of effective water chemistry control to tame the above problems. By modifying the corrosion and corrosion release behavior of carbon steel [4], the deleterious effects of corrosion and corrosion product transport in PHT system can be reduced significantly.

Enhancement of the protective nature of the oxide was attempted by external addition of Mg^{2+} as a passivating ion. Similar studies have been reported in literature for Boiling Water Reactor and Pressurised Water Reactor structural materials [5–7]. This paper gives an account of the studies carried out in re-circulating loop to explore the possibility of mitigating the corrosion of carbon steel in the presence of Mg^{2+}. Conventional methods like gravimetry and electrochemical techniques were adopted to quantify the extent of passivation. The magnesium ion uptake and oxide modification effected by Mg^{2+} was ascertained by several characterization techniques. The changes induced by Mg^{2+} in the morphology and electrical/transport properties of the corrosion product oxide were also investigated.

Controlling the corrosion and corrosion release of materials involves understanding of the mechanism of formation and stability of the corrosion product films on them. The corrosion reactions of the carbon steel involve various dynamic processes occurring at metal–oxide and inner oxide/solution interface. A better understanding of the various processes occurring during the film formation requires probing of the interfaces and processes as and when

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they are happening. This paper gives an account of the reduction in corrosion and release rates induced by Mg^{2+} addition, the presence of Mg^{2+} in the lattice of the oxide in chemically bonded form, the influence of Mg^{2+} modified oxide on the transport processes in the corrosion product film on carbon steel. The point defect model (PDM) was used to explain the perturbations caused by the incorporation of Mg^{2+} as a passivator and its role on the corrosion behavior of the carbon steel in high temperature aqueous media.

2. Materials and methods

2.1. Short term exposure – metal ion passivation loop

Carbon steel specimens for the experiment were cut from ASTM 106 Gr-B pipe. The elemental composition of the specimen estimated by radio frequency glow discharge optical emission spectrometry is given in Table 1. The specimens were ground to 800 grit, de-greased, washed with double distilled water, and exposed to simulated reactor water chemistry conditions. The specimens were arranged in specimen holders and exposed to high temperature simulated PHT conditions, of 290 °C and pH_{25} of 10.0 (0.7 ppm of Li as LiOH) in a re-circulating autoclave facility with a flow rate of 10 LPH. The system dissolved oxygen concentration was maintained at 10 ppb by continuously purging the low-pressure storage tank. Mg^{2+} was added to the system as magnesium acetate at a concentration equivalent to 200 ppb by weight magnesium at low temperature. The ion exchange purification column was isolated to avoid removal of added Mg^{2+} due to purification. The specimens were retrieved at the end of each exposure, washed with ultra pure water, dried and preserved in a desiccator for characterization studies.

2.2. Long term exposure – high temperature high pressure loop

The high temperature high pressure (HTHP) loop was used to simulate corrosion of structural materials under primary side water chemistry conditions. The operating conditions of the HTHP loop are given in Table 2.

Carbon steel specimens ground to 800 grade surface finish were degreased, cleaned with acetone, and used for the experiments. The specimens were loaded on a Teflon lined stringer and exposed in one of the test sections for six months. The specimens at the end of the experiment were used for further studies. The water, used contained about 10 ppb by weight of dissolved Mg^{2+}. The source of it was identified to be the dissolved Mg^{2+} from the magnesium oxide insulating material in the damaged surge tank immersion heater. The exposed specimens were retrieved and the oxide deposit was characterized.

Table 1
Composition of the carbon steel specimen.

Element	Composition (wt%)
C	0.22
Mn	0.52
Si	0.23
Cu	<0.04
Cr	<0.30
Mo	<0.03
Ni	<0.14
P	<0.01
V	<0.14
Co	<0.01
Sn	<0.01
S	<0.01

Table 2
HTHP loop operating conditions.

System volume	0.8 m^3
Flow	0.54 $m^3\ min^{-1}$
Temperature	288 °C
Pressure	11.03 MPa
Purification rate	0.003 $m^3\ min^{-1}$
Magnesium	10 ppb

2.3. Characterization of exposed specimens

SEM images of the exposed specimens were taken by using a PHILIPS ESEM XL-30 system. Raman spectra were recorded by using micro-Raman Spectrometer (LABRAM HR800) equipped with 514 nm argon ion laser. The laser was focused using 100× objective lens on sample surface with a laser power of 0.5 mW. 1800 groves/mm grating was used with a 30 s data acquisition time. X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHOIBOS 150 spectrometer (specs make) employing monochromatic Al Kα radiation at room temperature. The specimens were sputtered with argon ion beam, for 30–90 s, to remove carbon impurities.

Depth profiling and determination of the thickness of these metal oxide films on the specimens retrieved after long term exposure was carried out by direct current Glow Discharge Quadrupole Mass Spectrometry (GD-QMS). A quadrupole GD-MS, Model GQ230 (VG Elemental, UK), located in the Ultra Trace Analysis Laboratory at NCCCM, BARC, was used for the analysis.

2.4. In situ electrochemical studies

The experimental apparatus used in this study was an autoclave, of 1 L capacity, made of Hastelloy B, with provisions for doing high temperature electrochemical measurements. The apparatus consisted of facilities for precise temperature, pressure control, and facility for gas sparging. The test solution was pH 10.0 LiOH of specific conductivity 25 μS/cm at 25 °C, which was de-aerated by continuous purging with nitrogen gas. The dissolved oxygen was maintained below <10 ppb by initial nitrogen gas purging and venting at 85 °C. In some cases, 200 ppb of Mg^{2+} was added as magnesium acetate to the test solution. The autoclave was heated to 288 °C in three hours and the temperature was maintained at 288 ± 1 °C during the entire duration of the experiment. The autoclave was equipped with appropriate ports to accommodate working, counter, and reference electrodes, and with solution inlet and outlet ports. The rectangular carbon steel specimen surface was ground using successive grades of silicon carbide paper, finishing with 800 grit. Except the 1 cm^2 area of the carbon steel surface exposed to the solution, all the remaining surfaces were sealed with thin PTFE tape. The autoclave body was used as the counter electrode. An external Ag/AgCl (0.01 M KC1) electrode was used as reference electrode. A water jacket around the reference electrode body continuously cooled the Ag/AgCl end of the electrode to 25 °C [8]. A commercial potentiostat (Eco Chemie Autolab PG STAT30) was used to measure and control the potential, and a frequency response analyzer was used to measure the electrode impedance over the frequency range of 10 kHz to 5 mHz. An alternating current excitation potential, of 10 mV peak-to-peak, was used in the electrochemical impedance studies. The EIS spectrum was acquired in the presence and absence of 200 ppb Mg^{2+} (as magnesium acetate) as a function of time for 275 h. The carbon steel specimen was held at different anodic potentials and steady state current density was measured. Further, Mott Schottky studies were carried out on the specimen to characterize the passive oxide film formed.